Supplementary Material (ESI) for Chemical Communications

Supplementary Information

A mild deuterium exchange reaction of free carboxylic acids by photochemical decarboxylation

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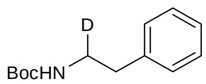
General

IR spectra were recorded on JASCO FT/IR-620. ^{1}H and ^{13}C NMR were recorded on JEOL JNM-AL500 (500 and 125MHz) and JEOL JNM-AL300 (300 and 75 MHz) spectrometers and for solutions in $CDCl_3$ containing TMS as an internal standard. High resolution mass spectra (HRMS) were obtained on JEOL JMS-700T. The light source was Riko UV-400HA 400-W high-pressure mercury lamp. Phen and DCB were recrystallized from hexane and EtOAc.

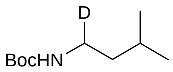
General Procedure for the Deuterium Exchange via Photochemical Decarboxylation

An acetonitrile-deuterium oxide solution (CH_3CN/D_2O = 98:2, CH_3CN 58.8 ml, D_2O 1.2 ml) of *N*-Boc-L-amino acid (**1**) (0.6 mmol, 10 mM), phenanthrene (Phen, 0.6 mmol, 10 mM), 1,4-dicyanobenzene (DCB, 0.6 mmol, 10 mM) and *t*-dodecanethiol (R'SH, 1.2 mmol, 20 mM) in four Pyrex (18 mm x 180 mm) was purged with argon for 5 min. The mixture was irradiated with 400-W high-pressure mercury lamp for 8. Then the solvent was evaporated, and the resulting residue was dissolved in EtOAc and washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to yield the corresponding deuterated product (**2**). Similar photoreaction of aliphatic acid (**3c-d**, **5**, **7**) (0.6 mmol, 10 mM), phenanthrene (Phen, 0.6 mmol, 10 mM), 1,4-dicyanobenzene (DCB, 0.6 mmol, 10 mM) and *t*-dodecanethiol (R'SH, 1.2 mmol, 20 mM) in a CH_3CN-D_2O solution (CH_3CN/D_2O = 9:1, CH_3CN 54 ml, D_2O 6 ml) in the presence of 1 equiv. NaOH (0.6 mmol, 10 mM) afforded the deuterated product (**4c-d**, **6**, **8**). These products were isolated by column chromatography on silica gel using hexane and EtOAc as eluents and by preparative HPLC using a GPC column or reversed phase column.

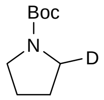
Characterization Data



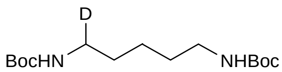
2a[1]: IR (KBr, cm^{-1}) 3357, 2962, 1701; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 4.53 (s (br), 1H), 3.40-3.36 (m, 1H), 2.80 (d, *J* = 6.7 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 139.0, 128.8, 128.5, 126.3, 79.2, 41.7, 36.2, 28.4; HRMS (FAB) calcd for $(M+H)^+$ $C_{13}H_{19}DNO_2$: 223.1557, found: 223.1550.



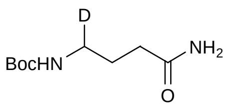
2b: IR (KBr, cm^{-1}) 3357, 2963, 1701; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (s (br), 1H), 3.12 (s (br), 1H), 1.63-1.57 (m, 2H), 1.44 (s, 9H), 0.91 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 79.0, 38.8, 28.4, 25.7, 22.5; HRMS (FAB) calcd for $(M+H)^+$ $C_{10}H_{21}DNO_2$: 189.1713, found: 189.1709.



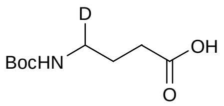
2c[2]: IR (KBr, cm^{-1}) 3339, 2961, 1699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33-3.28 (m, 3H), 1.82 (m, 4H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 78.9, 45.8, 28.5, 25.7; HRMS (FAB) calcd for $(M+H)^+$ $C_9H_{16}DNO_2$: 173.1400, found: 173.1347.



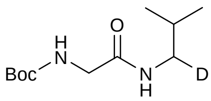
2d: IR (KBr, cm^{-1}) 3357, 2982, 1691; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (s (br), 2H), 3.13-1.10 (m, 3H), 1.59-1.56 (m, 2H), 1.50-1.30 (m, 22H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 79.0, 40.3, 29.7, 28.4, 23.8; HRMS (FAB) calcd for $(M+H)^+$ $C_{15}H_{30}DN_2O_4$: 304.2346, found: 304.2332.



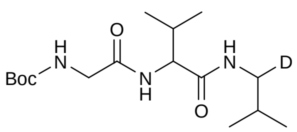
2e: IR (KBr, cm^{-1}) 3358, 3200, 2972, 1696, 1637; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (s (br), 1H), 5.40 (s (br), 1H), 4.75 (s (br), 1H), 3.20 (m, 1H), 2.28 (t, *J* = 6.8 Hz, 2H), 1.83 (q, *J* = 6.8 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 156.6, 79.4, 39.6, 32.8, 28.1, 25.7; HRMS (FAB) calcd for $(M+H)^+$ $C_9H_{18}DN_2O_3$: 204.1458, found: 204.1462.



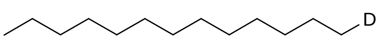
2f: IR (KBr, cm^{-1}) 3358, 2972, 1701; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (s (br), 1H), 3.17 (s (br), 1H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.84 (q, *J* = 7.1 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 156.2, 76.5, 39.4, 31.2, 28.3, 25.1; HRMS (FAB) calcd for $(M+H)^+$ $C_9H_{17}DNO_4$: 205.1298, found: 205.1296.



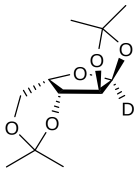
4a: IR (KBr, cm^{-1}) 3300, 2964, 1677, 1644, 1530; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (s, 1H), 5.14 (s, 1H), 3.77 (d, *J* = 6.1 Hz, 2H), 3.11-3.09 (m, 1H), 1.80-1.73 (m, 1H), 1.46 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 46.7, 46.5, 46.4, 46.2, 44.6, 28.2, 20.0; HRMS (FAB) calcd for $(M+H)^+$ $C_{11}H_{22}DN_2O_3$: 232.1771, found: 232.1794.



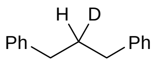
4b: IR (KBr, cm^{-1}) 3291, 2964, 1700, 1646, 1516; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (s, 1H), 5.12 (s, 1H), 3.78 (d, *J* = 6.7 Hz, 2H), 3.11-3.09 (m, 1H), 1.80-1.73 (m, 1H), 1.46 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 169.4, 58.7, 46.8, 30.5, 28.4, 28.3, 28.2, 20.1, 20.0, 19.3, 17.8; HRMS (FAB) calcd for $(M+H)^+$ $C_{16}H_{31}DN_3O_4$: 331.2455, found: 331.2434.



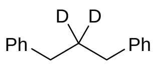
4c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31-1.23 (m, 24H), 0.89 (t, *J* = 7.0 Hz, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.9, 29.7, 22.7, 14.1.



4d[1, 3]: IR (KBr, cm^{-1}) 2962; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.51 (s, 1H), 4.29 (d, *J* = 2.1 Hz, 1H), 4.15-4.00 (m, 3H), 1.49 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.6, 105.2, 97.5, 84.7, 73.2, 71.6, 60.2, 28.9, 26.7, 26.1, 18.7; HRMS (FAB) calcd for $(M+H)^+$ $C_{11}H_{18}DO_5$: 232.1295, found: 232.1297.



6[4]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 5H), 7.19-7.16 (m, 5H), 2.65 (d, *J* = 7.6 Hz, 4H), 1.96-1.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 128.4, 128.3, 125.7, 35.4, 35.3; HRMS (FAB) calcd for $(M+H)^+$ $C_{15}H_{16}D$: 198.1393, found: 198.1385.



8[4, 5]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 5H), 7.19-7.16 (m, 5H), 2.64 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 128.4, 128.2, 125.7, 35.3, 35.2; HRMS (FAB) calcd for $(M+H)^+$ $C_{15}H_{15}D_2$: 199.1455, found: 199.1454.

References

1. Y. Yoshimi, T. Itou and M. Hatanaka, *Chem. Commun.* 2007, 5244.
2. (a) J.-C. Cintrat, F. Pillon and B. Rousseau, *Tetrahedron Lett.* 2001, **42**, 5001. (b) N. Faucher, J.-C. Cintrat and B. Rousseau, *Appl. Catal. A: Gen.* 2008, **346**, 86.
3. A. T. Khan and Md. Musawwer Khan, *Carbohydr. Res.* 2010, **345**, 154.
4. (a)K. A. De Castro, S. Oh, J. Yun, J. K. Lim, G. An, D. K. Kim and H. Rhee, *Synth. Commun.* 2009, **39**, 3509. (b) B. Štefane and S. Polanc, *Tetrahedron* 2009. **65**. 2339.
5. (a) D. Kuck and H.-F. Grützmacher, *Org. Mass Spectrom.* 1978, **13**, 90. (b) G. Boche, D. R. Schneider and K. Wernicke, *Tetrahedron Lett.* 1984, **25**, 2961.

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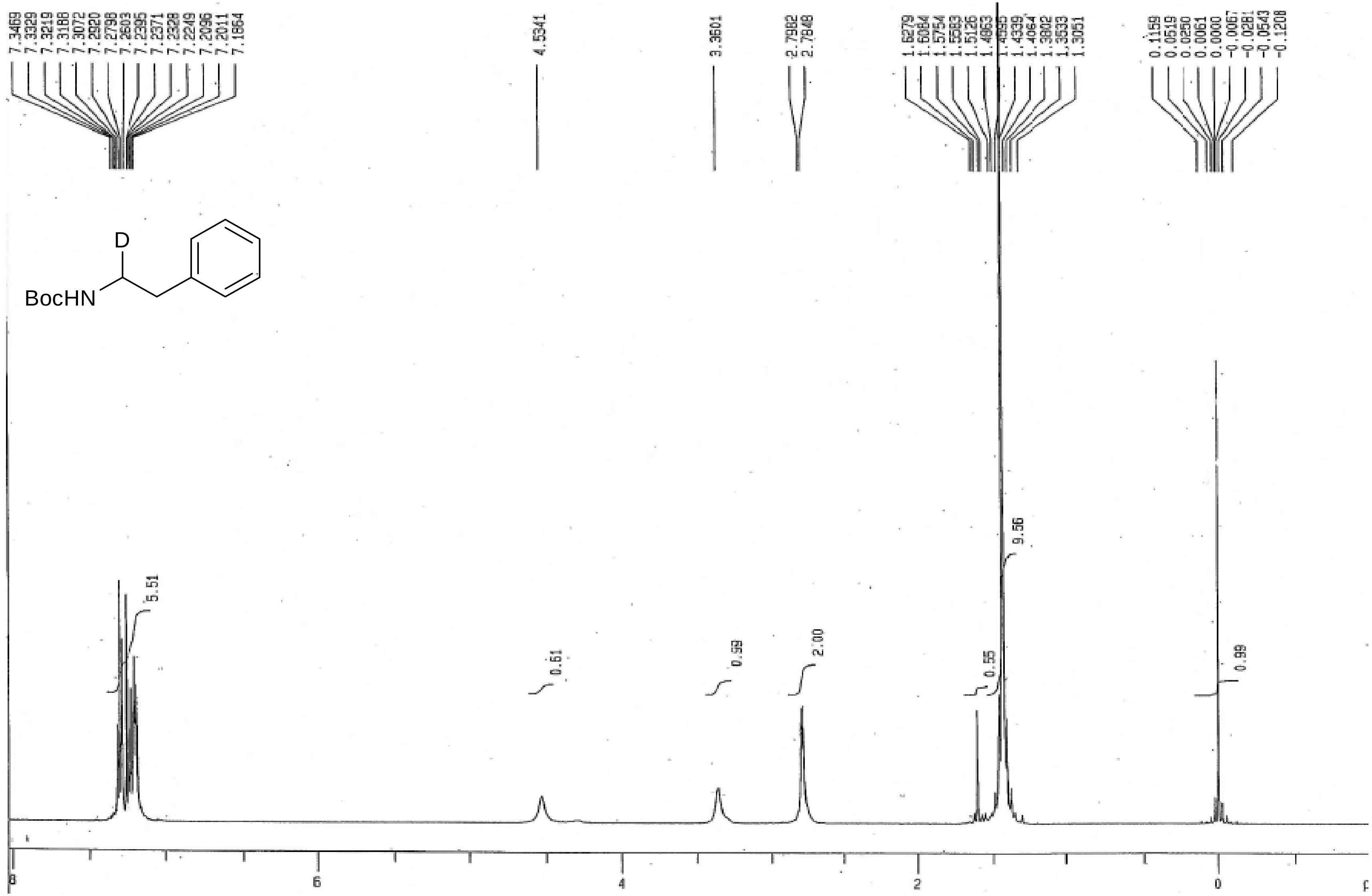

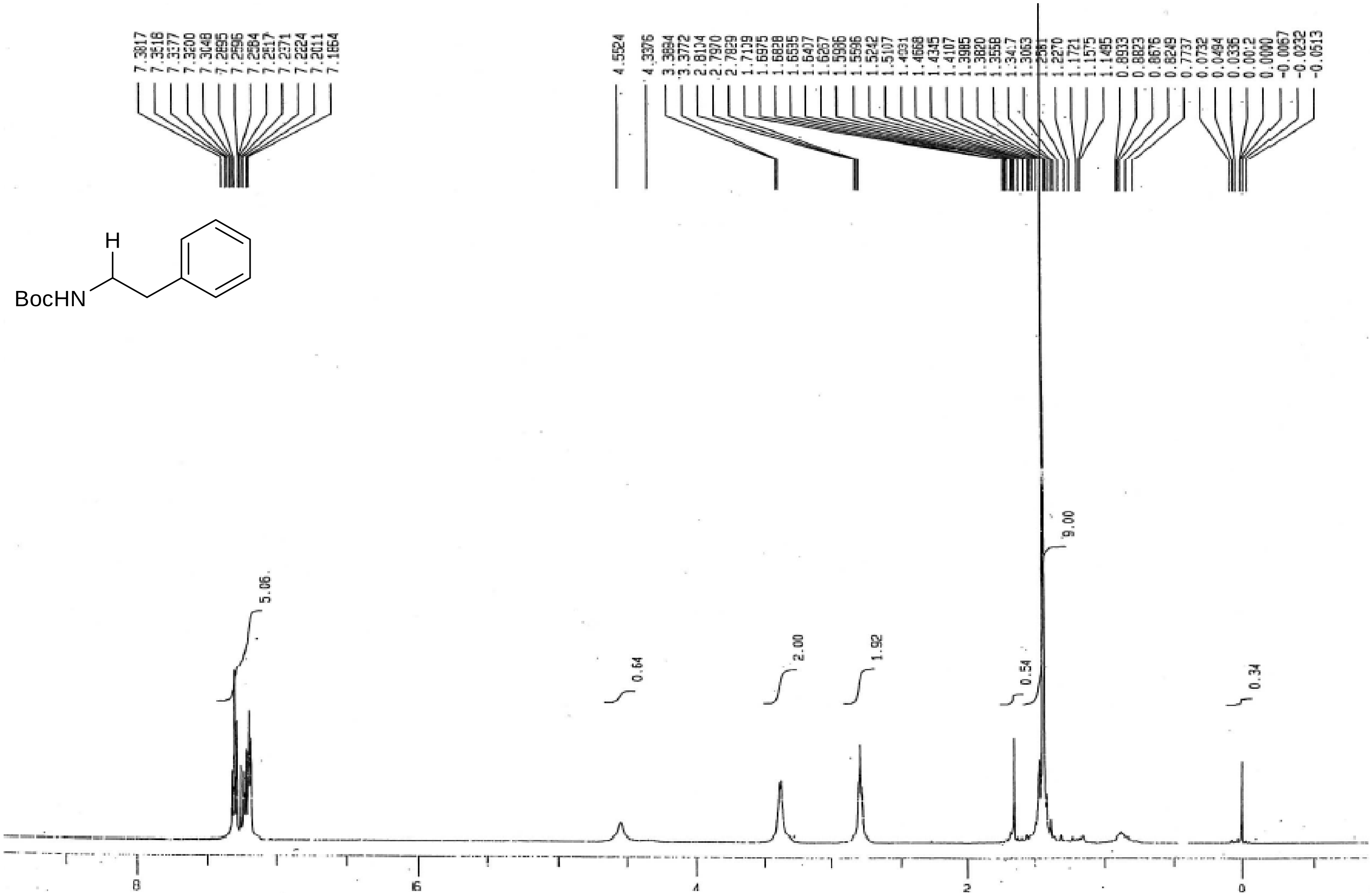
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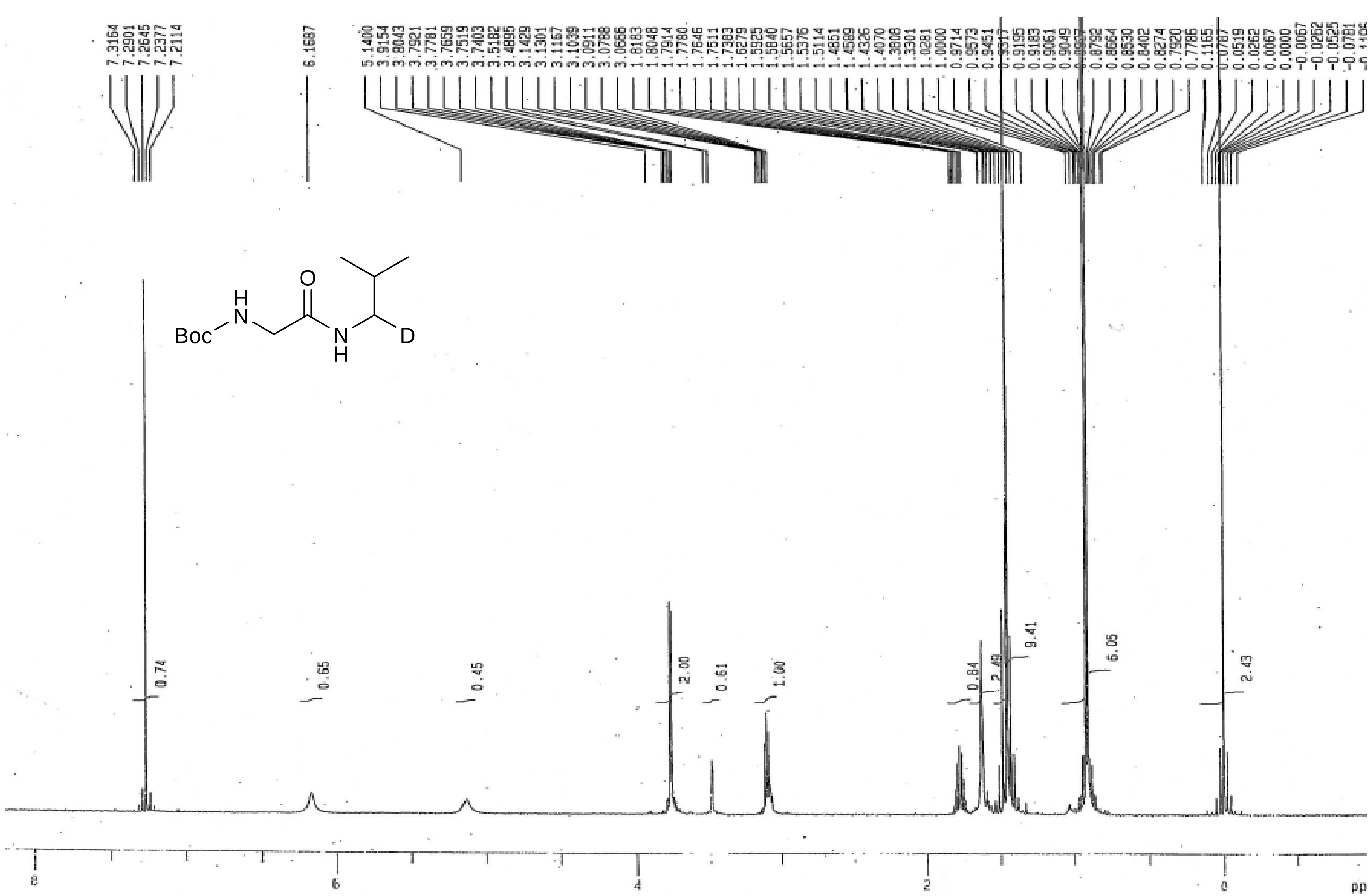
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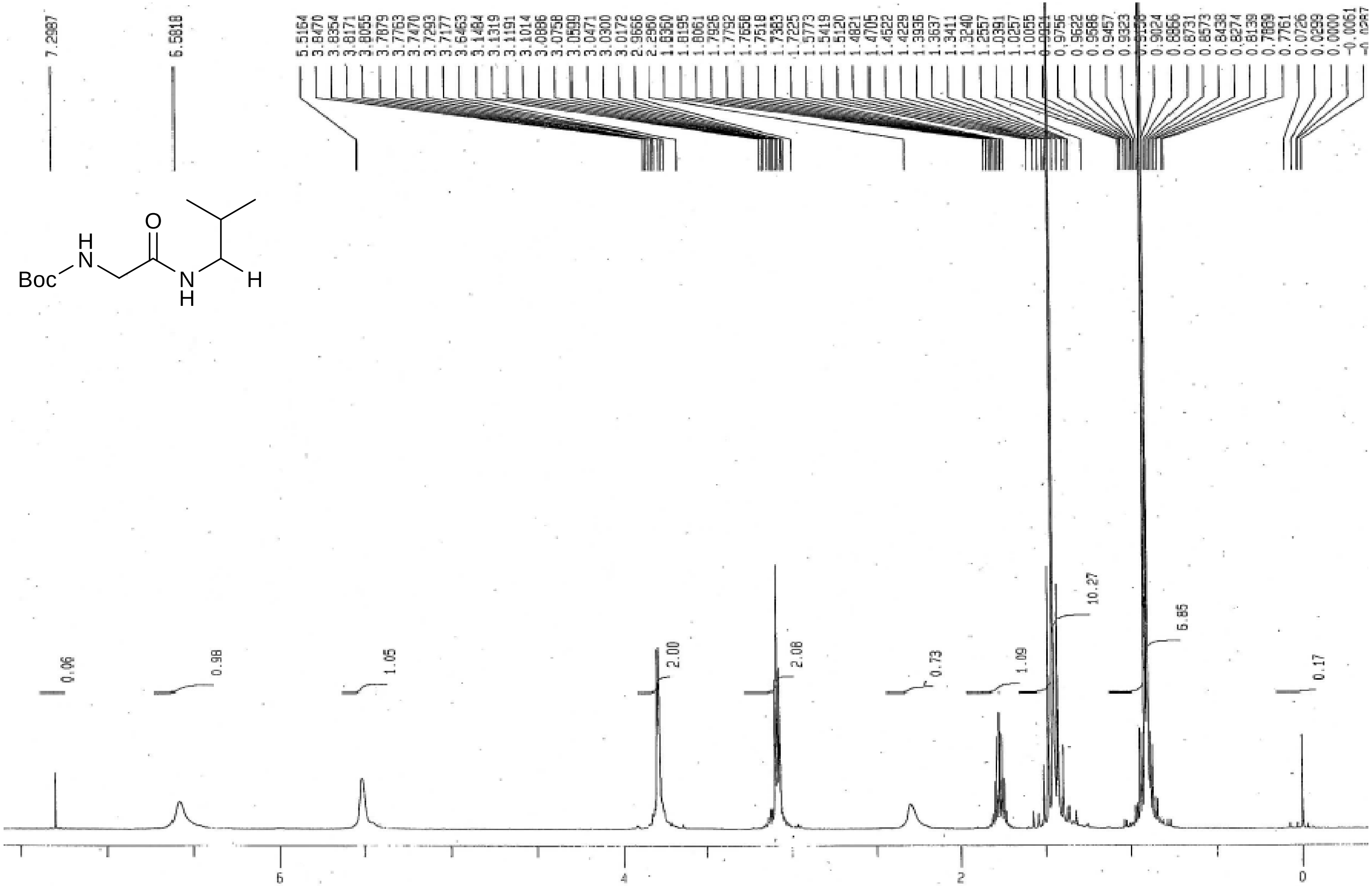
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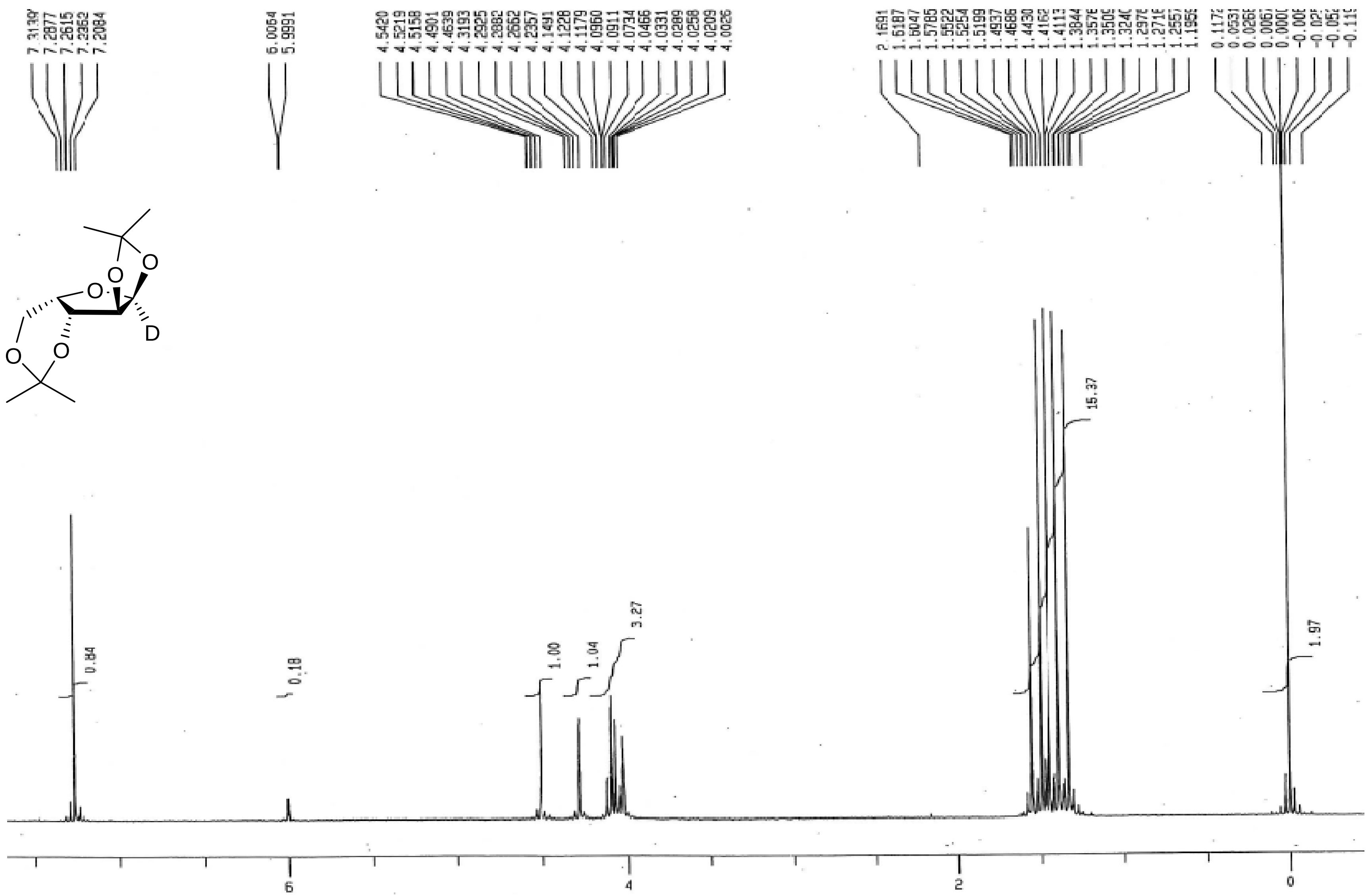
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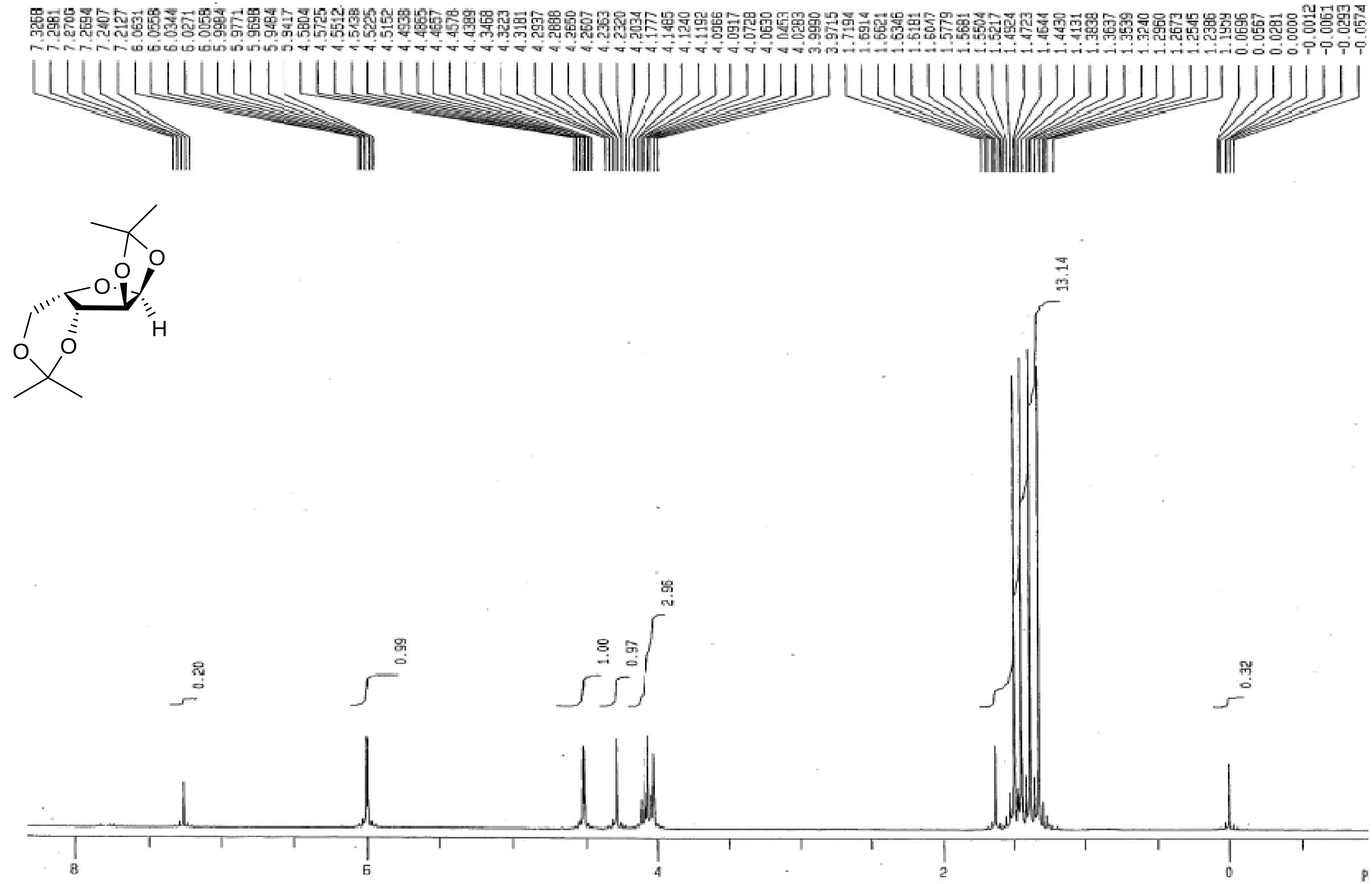
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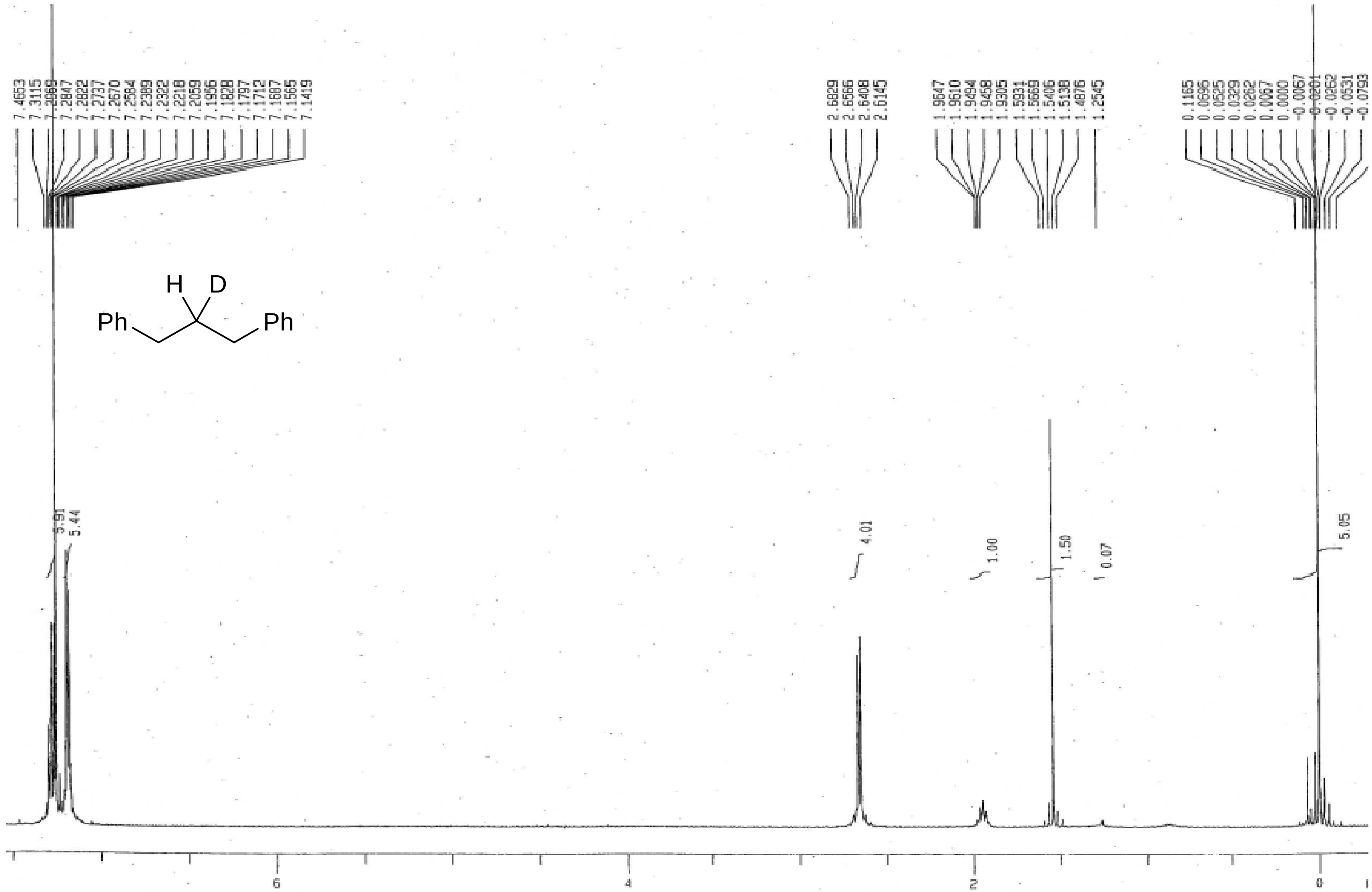

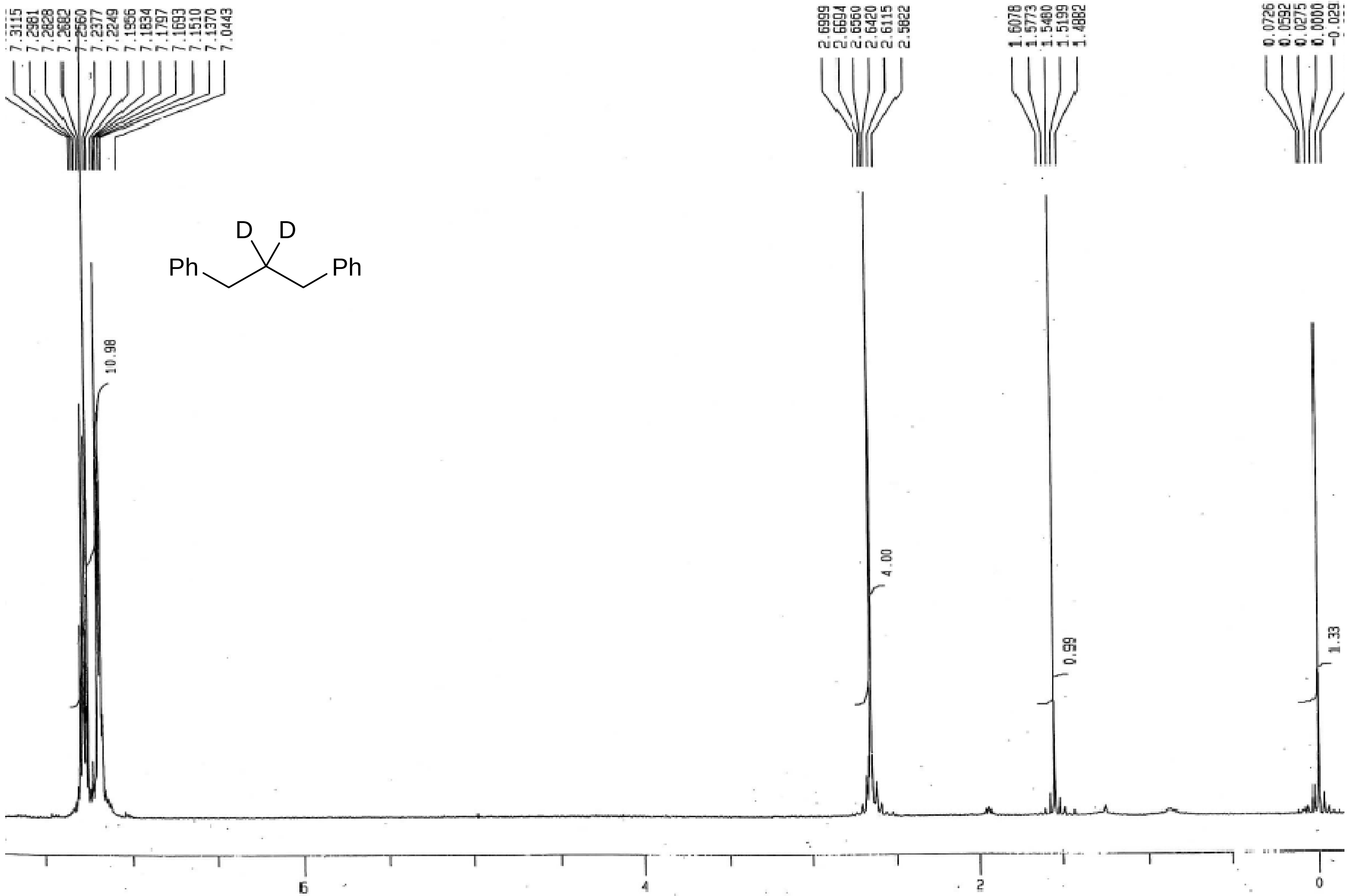
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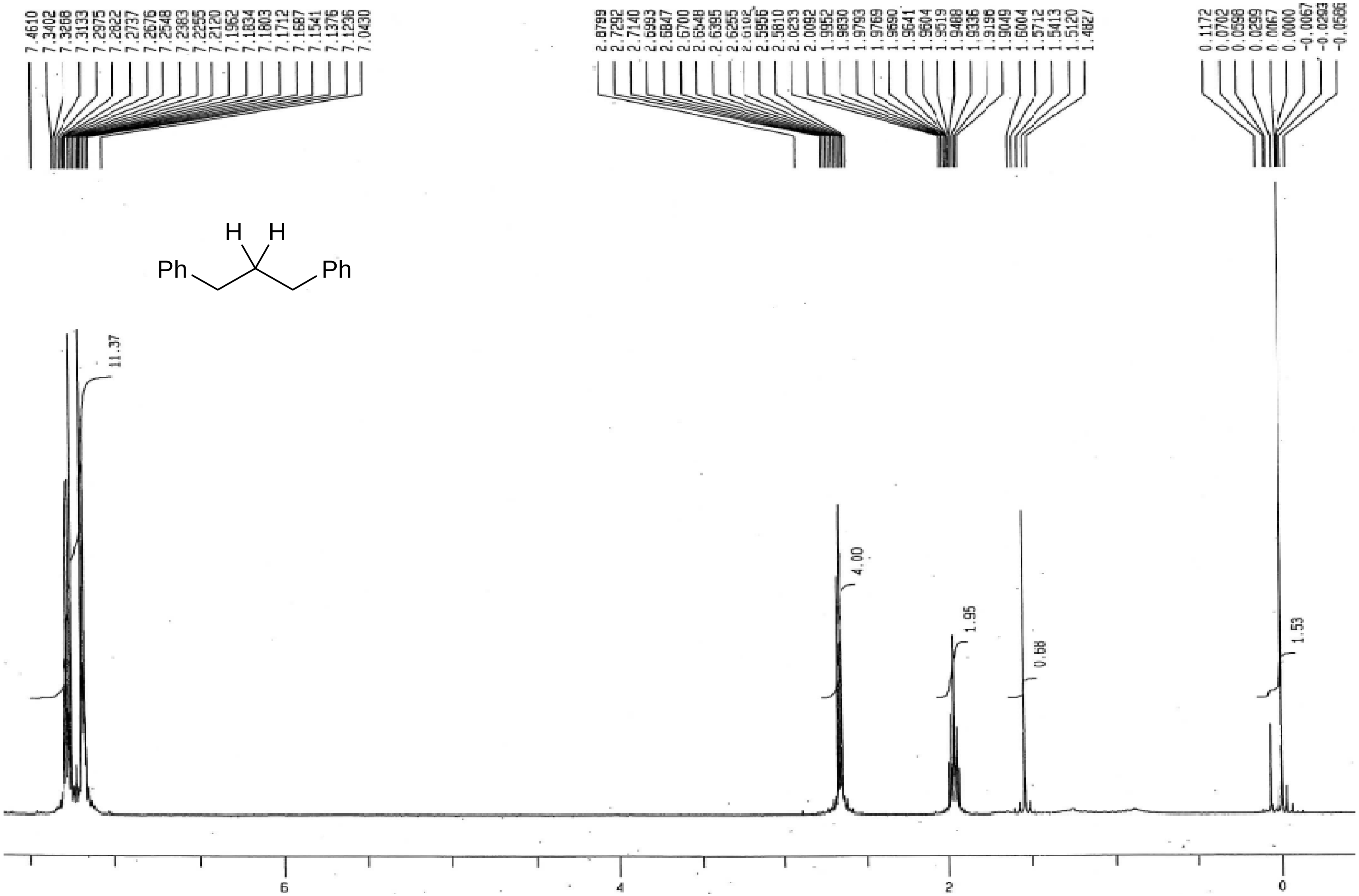
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